Bioresource Technology 144 (2013) 172–178

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Co-production of furfural and acetic acid from corncob using $ZnCl_2$ through fast pyrolysis in a fluidized bed reactor

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HIGHLIGHTS

- Corncob with $ZnCl_2$ was successfully pyrolyzed in a bench-scale fluidized bed.
- Relative response factor was applied for quantification of bio-oil components.
- The highest furfural yield was 8.2 wt% of the product.
- The highest acetic acid yield was 13.1 wt% of the product.

ARTICLE INFO

Article history:
Received 14 May 2013
Received in revised form 18 June 2013
Accepted 20 June 2013
Available online 28 June 2013

Keywords:
Furfural
Acetic acid
Corncob
Pyrolysis
Fluidized bed

ABSTRACT

Corncob was pyrolyzed using $ZnCl_2$ in a pyrolysis plant equipped with a fluidized bed reactor to co-produce furfural and acetic acid. The effects of reaction conditions, the $ZnCl_2$ content and contacting method of $ZnCl_2$ with corncob on the yields of furfural and acetic acid were investigated. The pyrolysis was performed within the temperature range between 310 and 410 °C, and the bio-oil yield were 30–60 wt% of the product. The furfural yield increased up to 8.2 wt%. The acetic acid yield was maximized with a value of 13.1 wt%. A lower feed rate in the presence of $ZnCl_2$ was advantageous for the production of acetic acid. The fast pyrolysis of a smaller corncob sample mechanically mixed with 20 wt% of $ZnCl_2$ gave rise to a distinct increase in furfural. A high selectivity for furfural and acetic acid in bio-oil would make the pyrolysis of corncob with $ZnCl_2$ very economically attractive.

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1. Introduction

Recently, the demand of fine chemicals has been increasing due to the rapid development of chemical industry. One of these fine chemicals is furfural which a platform chemical with a growing market. It has been widely used as a solvent, food additive and fungicide and also in the manufacture of pharmaceutical products, resins, and etc. (Lu et al., 2011a). In contrast to most conventional fine chemicals which are generally petroleum-based, furfural is exclusively produced from renewable biomass resources. Industrial furfural production is presently conducted by acid catalytic dehydration of pentosan-containing lignocellulosic materials in a batch or continuous reactor (Di Blasi et al., 2010a). Since this type of production method brings about tons of acid waste water, eco-friendly production methods have been passionately being researched. A promising alternative to the acid dehydration for the production of furfural is the pyrolysis of lignocellulosic biomasses consisting of cellulose, hemicelluloses, and lignin. Pyrolysis is a thermal process in the absence of oxygen. Recently, biomass pyrolysis focuses on the production of hydrocarbons by catalytic upgrading (Stefanidis et al., 2011) and it has also potential to produce value-added chemicals. It is well-known that furfural is produced from both of cellulose and hemicelluloses (Lu et al., 2011b). Corn residues such as corn stover and corncob have been usually used for the furfural production by pyrolysis (Ioannidou et al., 2009). In particular, corncob is the widely used feedstock for the furfural production due to its rich contents of pentosans and cellulose (Branca et al., 2010), although it can also be used for the production of bio-oil as a green fuel (Zheng et al., 2013). In a study on the non-catalytic pyrolysis of feedstocks with significant contents of cellulose/pentoses, furfural yields were in the range 2–0.8 wt%. (Di Blasi et al., 2010a). Demiral et al. conducted a series of experiments on a sample of corncob to determine the effects of pyrolysis parameters in the temperature ranges of 400–550 °C. In the experiments, the maximum oil yield of 26.4 wt% was obtained at a pyrolysis temperature of 500 °C, heating rate of 40 °C/min and sweeping gas flow rate of 100 cm^3/min (Demiral et al., 2012). In studies focusing on the production of furfural by pyrolysis, however, $ZnCl_2$ as a catalyst has been mostly applied. Encinar et al.

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0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.06.077

reported in an earlier study on the pyrolysis of grape and olive bagasse with $ZnCl_2$ that furfural concentration increased with temperature up to 600 °C, and then it decreased when temperature is further increased (Encinar et al., 1997). Recent researches continued to investigate the effect of $ZnCl_2$ on the furfural formation during pyrolysis. A study done by Di Blasi et al. revealed that $ZnCl_2$ was a particularly effective catalyst (concentrations of 1–6% and temperatures of 427–527 °C) to maximize the yield of furfural which was augmented by a factor of 5 and that a higher $ZnCl_2$ content, however, would cause the decreasing of the furfural formation (Di Blasi et al., 2008). Branca et al. conducted the pyrolysis of corncobs impregnated with variable amounts of $ZnCl_2$ and concluded that $ZnCl_2$ catalyzes the primary paths of furfural formation via dehydration of pentosyl and glucosyl residues (Branca et al., 2010). Amarasekara et al. investigated the effect of $ZnCl_2$ on the degradation of cellulose. The major non-gaseous products of the degradation of cellulose containing 0.5 mol of $ZnCl_2$/mol of glucose unit were furfural, 5-hydroxymethylfurfural and levulinic acid. The maximum yield for furfural was 8%, based on glucose unit of cellulose (Amarasekara and Ebede, 2009).

Meanwhile, some studies focusing on the production of acetic acid by pyrolysis were recently performed. Qi et al. performed the pyrolysis of bamboo over zeolite NaY and found that the content of acetic acid was the main component of bio-oil and its content is more than two times higher than that from a non-catalytic process (Qi et al., 2006). Lu et al. produced acetic acid of around 4 wt% by fast pyrolysis of biomass materials impregnated with $ZnCl_2$ in a small lab-scale equipment (Lu et al., 2011b).

Till now, most researches on the production of furfural and acetic acid were performed with Py-GC/MS or in a small scale apparatus. This study reports experimental results on the co-production of furfural and acetic acid from corncob with $ZnCl_2$ in a bench-scale fast pyrolysis plant equipped with a fluidized bed reactor having a capacity of up to 0.5 kg/h, which will give more practical aspects on the furfural production than ever. Main aim of this study is to find the effects of reaction conditions, the $ZnCl_2$ content and contacting method of $ZnCl_2$ with corncob on the yields of furfural and acetic acid. For a more reliable GC analysis, relative response factors (RRFs) for each component were calculated using the effective carbon number (ECN) and reference compounds. In addition, the quantification of furfural and acetic acid in the bio-oil was performed with the GC external standard method.

2. Experimental methodology

2.1. Feed material

The feed material, corncob, was obtained from a farm in Korea. It was first ground using a grinder, and then sieved to obtain two fractions of materials with a diameter 0.250–0.425 and 0.425–1 mm. The two fractions were then dried in an oven at 105 °C for 72 h and were then used in each operation. Main characteristic of the corncob is shown in Table 1.

Proximate analysis showed that the feed material had a high content of volatile matter (88.1 wt%). The ash content was also relatively high (8 wt%). Ultimate analysis showed that it was mainly composed of carbon and oxygen. The content of holocellulose (cellulose and hemicelluloses) amounted to about 61 wt%.

Contacting of $ZnCl_2$ with corncob was accomplished by two methods, a mechanical mixing and wet impregnation. The mechanical mixing was a manual mixing of corncob and $ZnCl_2$ with a stirrer. After the mechanical mixing, the mixture was charged in the silo of the plant. The wet impregnation of $ZnCl_2$ on corncob was achieved as follows: First, 100 g of corncob whose particle size was 0.250–0.425 mm was soaked in a 1 l $ZnCl_2$ aqueous solution and then stirred for 3 h. Finally, the impregnated material was dried in oven at 75 °C for 72 h.

Table 1
Characteristics of feed material.

Proximate analysis (wt%)[a]		Ultimate analysis (wt%)[b]	
Moisture	2.8 ± 0.01	Carbon	43.3 ± 0.01
Volatile matter	88.1 ± 1.8	Hydrogen	5.5 ± 0.00
Fixed carbon	1.1 ± 0.16	Nitrogen	0.9 ± 0.11
Ash	8 ± 1.64	Oxygen[c]	50.3
		Sulfur	–
Chemical composition (wt%)			
Cellulose	27.5 ± 1.68	Hemicelluloses	33.6 ± 4.2
Lignin	19.6 ± 0.39	Extractives	14.3 ± 0.39

[a] Wet basis.
[b] Dry and ash free basis.
[c] Calculated by difference.

2.2. Fast pyrolysis plant

The fast pyrolysis plant was composed of a feeding system, fluidized bed reactor, char separation system, quenching system and product gas circulation system. A diagram of the plant is shown in Fig. 1.

The key part of the plant was the fluidized bed with a height of 390 mm and an inner diameter of 110 mm, which was made of a 316 SS tube. To monitor the reaction temperature and fluidization behavior during pyrolysis, three thermocouples were installed inside the reactor. The pyrolysis reaction temperature was determined by the average value of the three thermocouples. The fluidized bed reactor was heated indirectly in an electric heater (4.5 kW). The feeding system was comprised of two screw feeders which helped load material uniformly and directly into sand in the fluidized bed. To avoid a reflow of pyrolysis vapor into the feed system, part of the product gas was introduced into the silo and feeder during experiment. The char separation system was composed of a cyclone and ceramic hot filter designed to capture particle bigger than 10 and 2 μm, respectively. The quenching system consisted of one water-cooled steel condenser and two ethanol-cooled glass condensers, which operated at 20 and −25 °C, respectively. To capture aerosols, an electrostatic precipitator behind the condensers was used. Part of the product gas was either burned in a stack to regulate the pressure in the plant or was used for gas sampling. Much of the product gas was circulated into the fluidized bed reactor through a pre-heater using a compressor (N0150ATE, KNF) for fluidization.

2.3. Reaction conditions

In each experiment, the input of the feed material was 100 g, and 2.6 kg quartz sand with a mean diameter of 0.25 mm was used as the fluidized bed material. The feed rate was about 2–4 g/min, and the product gas was used for the fluidizing medium. To maintain a constant residence time of pyrolysis vapor in the reactor, the flow rate of product gas (33–38 NL/min) was corrected with respect to the reaction temperature. Main reaction conditions are shown in Table 2.

Reaction parameters were reaction temperature, feed size, and feed rate. When $ZnCl_2$ was applied, the effects of the $ZnCl_2$ content and contacting method of $ZnCl_2$ with corncob on the yields of furfural and acetic acid were investigated. Runs 1 to 6 were performed with a corncob with a diameter 0.425–1 mm; whereas Runs 7 to 10 with a diameter 0.250–0.425 mm. To see the influence of reaction temperature on the product spectrum, Runs 1 to 3 were conducted; to find the influence of $ZnCl_2$ content in the mechanical mixing, Runs 4 and 5 were carried out for comparison with Run

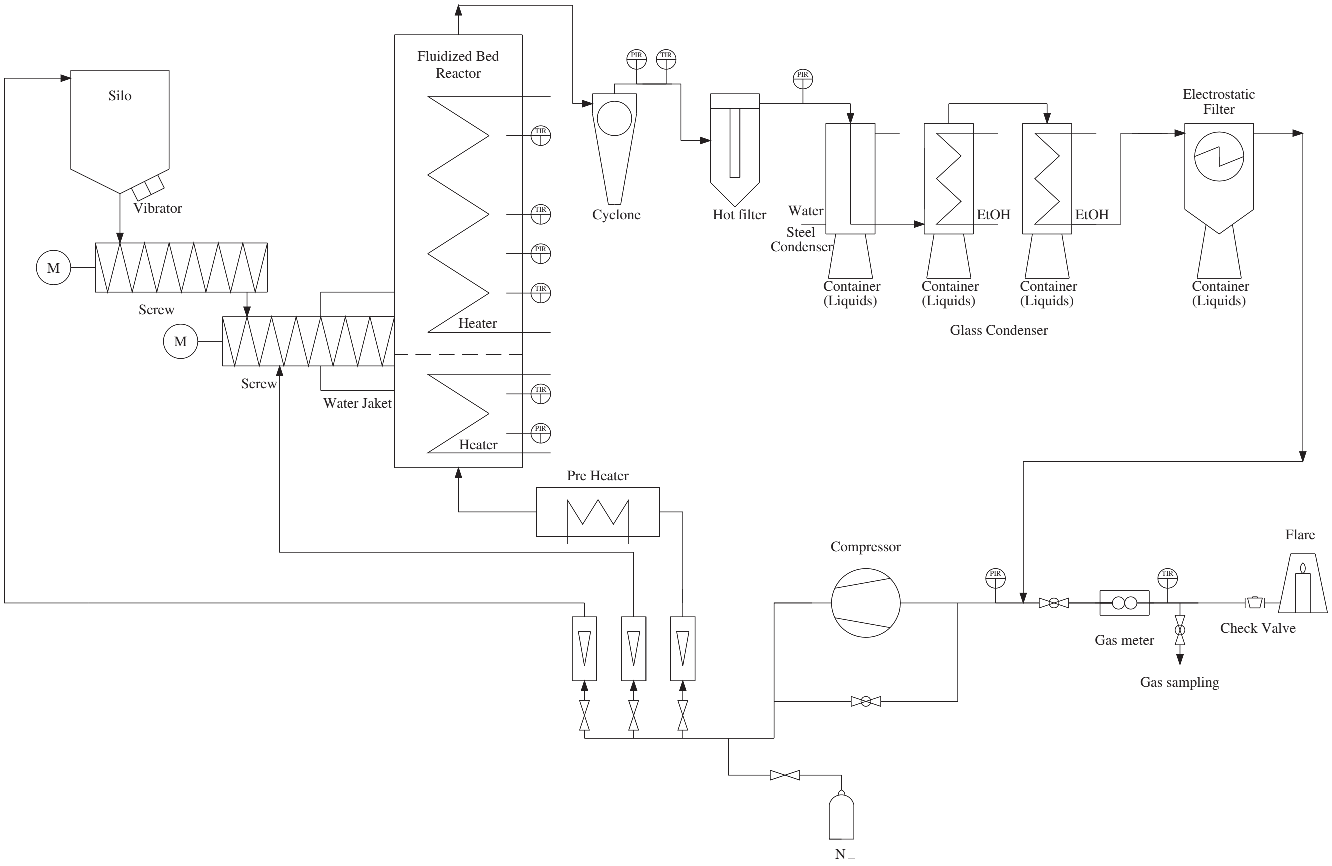

Fig. 1. Diagram of the fast pyrolysis plant. (This figure shows the details of the fast pyrolysis system).

Table 2
Reaction conditions.

Parameter	Run1	Run2	Run3	Run4	Run5	Run6	Run7	Run8	Run9	Run10
Reaction temperature (°C)	311	357	411	356	358	353	355	347	345	351
Feed rate (g/min)	2	2	2	2	2	4	2	4	4	4
Flow rate (NL/min)	38	36	33	36	36	36	36	36	36	36
Feed size (mm)	0.425–1						0.250–0.425			
$ZnCl_2$ (wt%)	0	0	0	10[a]	20[a]	20[a]	0	10[b]	20[b]	20[a]

[a] Mechanical mixing.
[b] Wet impregnation.

2; to determine influence of feed rate, Run 6 was carried out for comparison with Run 5; and to find out the effect of the feed size without catalyst, Runs 7 was performed for comparison with Runs 2. Runs 8 and 9 were conducted to find the influence of $ZnCl_2$ content in the wet impregnation. Run 10 was performed to confirm the feed size effect with mechanically mixed $ZnCl_2$, the result of which can be compared with that of Run 5.

2.4. Analysis of products

Pyrolysis products were divided into three fractions: bio-oil, gas and char. The water content of each bio-oil was measured using a Karl Fischer titrator (Metrohm 870, KF Titrino) with HYDRANAL Composite 5 K (Riedel-de Haen) as the titration regent and methanol as the titration solvent. Bio-oil was qualitatively and quantitatively analyzed by comparing the peaks obtained by a GC-FID (7890 A, Agilent Instruments) and a GC–MS (5975 C, Agilent Instruments). The column employed for both GC-FID and GC–MS was a HP-5MS (30 m × 250 mm i.d., 0.25 μm film thickness), with helium used as the carrier gas. For the quantitative analysis, ECN of each compound was calculated according to a reference (Scanlon and Wills, 1985). The RRF of each compound was calculated using ECN and a reference compound. The RRF was determined according to the following Eq. (1).

$$\text{RRf of substance A} = \frac{\text{ECN of reference compound} \times \text{molecular weight of A}}{\text{Molecular weight of reference compound} \times \text{ECN of A}} \tag{1}$$

Finally, each peak area was multiplied by a RRF to give a corrected peak area. For the qualitative analysis, compounds were identified on the basis of a typical MS library (Wiley7nist05), selecting only the compounds showing matches higher than 80% possibility. For the quantification of furfural and acetic acid in bio-oil, a calibration curve for each compound was established using standard solutions. The concentration of each compound in a bio-oil sample could be graphically determined. The R^2 values of calibration curves were 0.9983 for acetic acid and 0.9949 for furfural, respectively. The pyrolysis gases were analyzed offline using

GC-TCD and GC-FID (7890A, Agilent Instruments), with argon as the carrier gas. The columns that were applied were Carboxen 1000 (TCD) and HP-plot Al_2O_3/KCl (FID). $ZnCl_2$ concentration in the substrate after wet impregnation was determined by an ICP-AES (ICPE-9000, Shimadzu). A series of thermogravimetric analyses of corncob samples were performed with a thermogravimetric analyzer (TGA Q50, TA Instruments) under a nitrogen atmosphere. The sample amount used in the experiment was 10–20 mg. Each of the samples was heated in a platinum pan within the temperature range between 30 and 800 °C with various heating rates of 5, 10 and 20 °C/min of 100 ml/min.

3. Results and discussion

3.1. TGA experiments

TGA experiments were conducted with corncob samples at different heating rates. In the experiments, the temperature range at which weight loss took place increased, as the heating rate increased. The main thermal degradation took place within the range 150–400 °C. The corncob sample had two distinct decomposition regions. A previous study reported that the main degradation of hemicelluloses occurred at 220–315 °C; that of cellulose was mainly happened at 315–400 °C; and that of lignin covered the temperature range between 150 and 900 °C (Yang et al., 2007). Therefore, the first weight loss of the two regions seemed to be primarily due to the decomposition of hemicelluloses, which continued up to 250 °C. The second region up to 400 °C appeared to be mainly due to cellulose decomposition. Based on the TG (or DTG) curves, the temperature range 300–410 °C was chosen as the reaction temperature range of the pyrolysis in the fluidized bed reactor, because the maximum yields of furfural and acetic acid that originate mainly from hemicelluloses and partly from cellulose were aimed in this study.

3.2. Product distribution

In all fast pyrolysis experiments, mass balances were established on an as received basis. In each mass balance, the gas yield was obtained by multiplying the gas volume produced in the experiment and the gas density obtained from the gas composition. Pyrolysis oil yield was obtained by weighing the oils captured by condensers and electrostatic precipitator. Finally, the char yield obtained without $ZnCl_2$ was calculated by difference between the feed and gas plus oil amounts. It was reported that the use of $ZnCl_2$ in pyrolysis caused the emission of chlorinated volatile organic compounds (VOCs) which could exist in gas and oil (Chiang et al., 2012). The char yield obtained with $ZnCl_2$ included the $ZnCl_2$ amount remained in the char after pyrolysis. Therefore, direct comparisons of between product yields from the experiments with and without $ZnCl_2$ in mass balances should be avoided. Table 3 shows product mass balances of the experiments.

As shown in Table 3, the bio-oil yield was 30–60 wt% of product. In the case of the bio-oils obtained without $ZnCl_2$, the bio-oil yield was between 48–58 wt% with the water content of about 57 wt%. Because the fast pyrolysis from Runs 1 to 3 was conducted at relatively low temperatures (between 310–410 °C) compared with that of typical fast pyrolysis of biomass (around 500 °C), the bio-oil appeared to be rich in water and decomposition products of hemicelluloses and celluloses. Table 3 reveals that increasing temperature (from Runs 1 to 3), a smaller feed size (comparisons between Run 2 and Run7 and between Run 6 and Run 10), and a higher feed rate (comparison between Run 5 and Run 6) favored for the production of bio-oil. At higher temperatures, the devolatilization of corncob would be enhanced to make the oil yield higher. Small particles increased the bio-oil yield due to the good heat transfer to the inner side of the feed. A higher feed rate would cause a short residence time of pyrolysis vapor, decreasing the potential for secondary cracking and the resultant formation of gaseous product. This result is in good agreement with previous studies (Jung et al., 2012; Kim et al., 2010). With increasing temperature within the range between 310–410 °C, the gas yield increased mainly due to the secondary cracking of pyrolysis vapor at higher temperatures. With increasing of the $ZnCl_2$ amount in both mechanical mixing and wet impregnation methods, the bio-oil yield distinctly decreased; whereas the char yield increased. The main reasons for the increase in the char yield appeared to result from on one hand that most of $ZnCl_2$ remained in the char product, and on the other hand, that $ZnCl_2$ would catalyze the charring reactions (Di Blasi et al., 2010b; Di Blasi et al., 2008). As the $ZnCl_2$ content increased in both the mechanical mixing and wet impregnation methods, the water content in bio-oil increased; whereas organic liquid in bio-oil decreased. The results revealed that $ZnCl_2$ inhibited the formation of organic liquid acting as a dehydrating agent (Lu et al., 2011b).

3.3. Bio oil

Table 4 is the analytical results of GC/MS and GC-FID of bio-oils obtained from Runs 1 to 3 where the influence of temperature on the concentrations of bio-oil compounds without $ZnCl_2$ was investigated.

As shown in Table 4, the bio-oils consisted mainly of acetic acid, hydroxyacetic acid, furfural and hydroxyacetone. The acetic acid concentration in bio-oil, which was highest among GC detectable components, linearly increased from 33.1 to 38.5 wt% with increasing reaction temperature. The acetic acid concentration seemed to be much higher, compared with that reported by a study, where the acid content lay between 2.3–3.5 wt% for energy crops and between 0.5–12 wt% for typical wood (Mullen and Boateng, 2008). The main reasons for the high acetic acid concentration in this study would lie in on one hand that the feed material in this study was corncob which was abundant in hemicelluloses that could produce acetic acid by deacetylation during pyrolysis, and the other hand that the fast pyrolysis was conducted at lower reaction temperatures where lignin fraction of corncob could not be sufficiently devolalitized to be components of bio-oil. A recent study on the fast pyrolysis of corn stalk in a fluidized-bed reactor reported that the bio-oil contained 27.3% acetic acid (Pittman et al., 2012).

Table 3
Mass balances from the pyrolysis of corncob on as received basis.

Products (wt%)	Run1 (311 °C)	Run2 (357 °C)	Run3 (411 °C)	Run4 (356 °C)	Run5 (358 °C)	Run6 (353 °C)	Run7 (355 °C)	Run8 (347 °C)	Run9 (345 °C)	Run10 (351 °C)
Oil	48.2	52.7	58.3	46.3	29.8	46.6	59.0	60.0	48.1	47.8
(Water)	(57)	(57)	(56.9)	(62.4)	(68.1)	(70.1)	(57.1)	(63.1)	(70.4)	(68.8)
Gas	17.7	21.5	24.3	16.8	14.9	15.3	17.7	10.0	10.1	11.4
Char	34.1	25.8	17.4	36.9	55.3	38.1	23.3	30	41.8	40.8

Table 4
Concentrations of main compounds of bio-oils.

Compounds	ECN	RRF	Concentration (wt%)		
			311 °C	357 °C	411 °C
1-Propanol	2.5	0.54	1	1.2	1.3
Butanedione	2	0.97	1	1.2	1.2
Cyclopentanol	4.5	0.43	1	1.1	0.9
Acetic acid	1	1.36	33.1	33.4	38.5
Hydroxyacetone	1.5	1.12	9.6	7.4	7.9
Propanoic acid	2	0.84	0.1	0.5	0.5
1-Hydroxy-2-butanone	2.5	0.80	3.2	1.2	0.9
Methyl acetate	1	1.67	0.6	2.7	2
Methyloxirane	2	0.66	1.3	1.3	1
Furfural	2.8	0.78	3.5	6.4	5.5
Furfuryl alcohol	3.8	0.58	4.4	3.1	1.7
5-methyl-2(3*H*)-furanone	2.9	0.76	0.1	0.1	–
Ethylene acetate	2	1.65	–	2	–
2-cyclopentene-1,4-dione	2.9	0.75	0.2	0.2	–
1-(2-furanyl)-ethanone	3.8	0.65	0.2	0.2	0.2
Dihydro-2(3*H*)-furanone	3	0.65	0.4	0.4	0.3
2(5*H*)-Furanone	1.9	1	0.9	1.1	0.9
1,2-Cyclopentanedione	3	0.74	3	3	2.1
Corylon	4.9	0.52	0.5	0.7	0.7
5-Methyl-Furfural	3.8	0.65	0.4	0.4	0.5
3-Methyl-2-cyclopentenone	4.9	0.44	0.04	0.1	0.1
1-Acetoxy-2-butanone	3	0.98	0.3	0.3	0.2
3-Methyl-2(5*H*)-furanone	2.9	0.76	0.2	0.2	0.1
Phenol	6	0.35	0.5	0.5	0.4
m-Cresol	7	0.35	0.1	0.1	–
p-Cresol	7	0.35	–	0.2	0.3
Guaiacol	6	0.47	0.7	0.7	0.7
Maltol	4.8	0.59	0.2	0.2	0.2
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	5.4	0.53	0.2	0.2	0.2
2,3-Dihydroxybenzaldehyde	6	0.52	0.1	0.1	0.1
p-Ethyl-phenol	8	0.35	0.3	0.3	0.3
p-Creosol	7	0.45	0.1	0.2	0.2
Pyrocatechol	6	0.41	0.7	0.6	0.8
4-Methylbenzaldehyde	7	0.39	2.7	2.1	1.7
4-Vinylphenol	7.9	0.34	1.4	0.9	0.7
5-(Hydroxymethyl)furfural	3.8	0.75	1.2	0.9	1.2
3-Methoxy-pyrocatechol	6	0.53	0.2	0.3	0.2
3-Methyl-pyrocatechol	7	0.40	0.1	0.1	0.1
p-Ethylguaiacol	8	0.43	0.3	0.3	0.2
Hydroquinone	6	0.41	0.1	0.2	0.2
p-Vinylguaiacol	5	0.68	3.3	2.6	2.4
p-Formylphenol	6	0.46	0.1	0.1	0.1
Vanillin	6	0.57	0.2	0.2	0.2
Levoglucosan	1.75	2.09	1.9	3.0	4.3
Methoxyeugenol	5	0.88	0.6	0.4	0.6
Unknown			19.96	17.6	18.4
Sum			100	100	100

(–) : Not detected.

The furfural concentration in the bio-oils was between 3.5 and 5.5 wt%, showing the maximum yield obtained at 357 °C. The concentration of furfuryl alcohol, which is manufactured industrially by the catalytic reduction of furfural and is widely used as a solvent or as an ingredient in resin production, decreased with respect to reaction temperature, showing its range 1.7–4.4 wt%.

3.4. Effects of reaction parameters on the furfural and acetic acid yields

Pyrolysis parameters and the use of $ZnCl_2$ would significantly affect the production of furfural and acetic acid. To identify their effects, the GC analysis of bio-oil with the external standard method was performed. Fig. 2 shows concentrations of furfural and acetic acid in bio-oil with respect to reaction temperature, the $ZnCl_2$ content and contacting method of $ZnCl_2$ with corncob, respectively.

As shown in Fig. 2(a) which shows the influence of reaction temperature in the absence of catalyst, the furfural concentration increased, then maximized and then decreased, as the reaction temperature rose from 311 to 411 °C. The maximum furfural concentration was 1.5 wt% of bio-oil. With increasing reaction temperature, the acetic acid concentration was gradually increased. The maximum acetic acid concentration was about 21.2 wt%. There were differences in concentrations of the two compounds between the GC-FID analysis and the external standard method, mainly due to the exclusion of water content in bio-oil in GC-FID analysis. The concentration trends for the two components with increasing temperature, however, were the same as the GC data seen in Table 4.

Fig. 2(b) shows the effects of the $ZnCl_2$ amount and contacting method of $ZnCl_2$ with corncob on the concentrations of furfural and acetic acid. A previous study reported that the presence of $ZnCl_2$, which is a Lewis acid, inhibited the devolatilization of lignin and pyrolytic ring scission of holocellulose; while it promoted the depolymerization and dehydration of holocellulose to form furfural (Lu et al., 2011a). First, in regard to contacting method of $ZnCl_2$ with corncob, it is clearly seen in Fig. 2(b) that the furfural concentration was much higher with the impregnated corncob, compared with the mechanical mixing method. This is mainly because the actual amount of $ZnCl_2$ playing a catalytic role would be higher in the case of the impregnated corncobs, when the same amount of $ZnCl_2$ was applied for both the methods. The $ZnCl_2$ concentration in the substrate after the wet impregnation method was investigated by ICP-AES. The analysis revealed that about 91.5–97 wt% of $ZnCl_2$ was actually attached on the corncob during wet impregnation. The high $ZnCl_2$ amount would be possible due to the low intrinsic particle density of corncob, which enabled corncob to have better

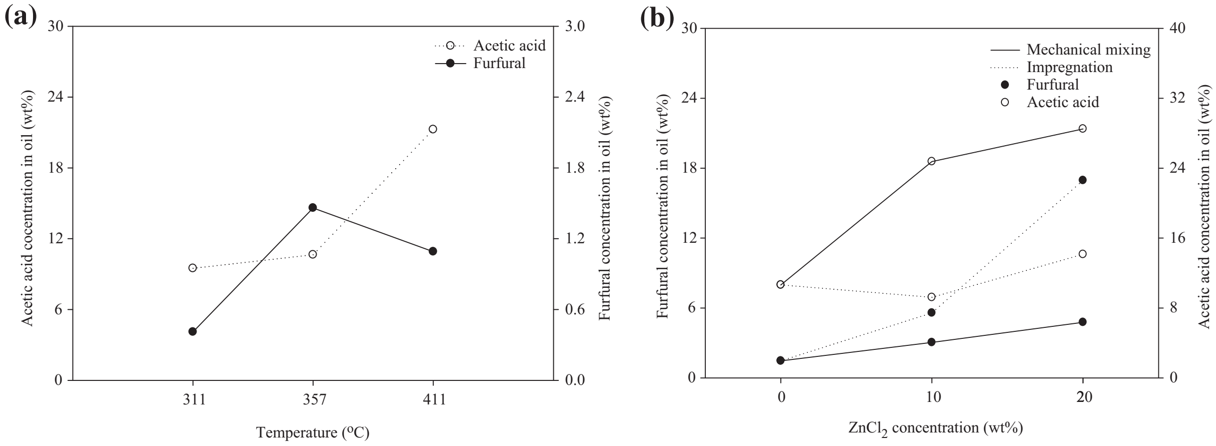

Fig. 2. Effect of (a) reaction temperature and effects of (b) $ZnCl_2$ concentration and contacting method.

Table 5
Yields of furfural and acetic acid with respect to the reaction parameters.

Yield (wt%)	Run1 (311 °C)	Run2 (357 °C)	Run3 (411 °C)	Run4 (356 °C)	Run5 (358 °C)	Run6 (353 °C)	Run7 (355 °C)	Run8 (347 °C)	Run9 (345 °C)	Run10 (351 °C)
Furfural	0.2	0.8	0.6	1.4	2	2.6	0.6	3.4	8.2	4
Acetic acid	4.6	6.2	9.9	10.4	13.1	7.8	7.9	5.5	8.4	7.4

impregnation properties. It is also seen in Fig. 2(b) that the furfural concentration also increased with increasing the $ZnCl_2$ content. In particular, the furfural concentration in the bio-oil of Run 9, where a corncob impregnated with 20 wt% of $ZnCl_2$ was pyrolyzed, reached up to about 17 wt% of bio-oil. A similar furfural content in bio-oil which was obtained with a corncob impregnated with about 18 wt% of $ZnCl_2$ was reported in a study (Lu et al., 2011b).

In the case of acetic acid, its concentration in bio-oil was higher and tended steadily to increase with the increasing $ZnCl_2$ content in both the preparation methods. The highest acetic acid concentration (28.5 wt%) was surprisingly achieved in Run 5 where 20 wt% of $ZnCl_2$ was mixed with corncob by the mechanical method. The acetic acid concentration in bio-oils produced by the wet impregnation method was much lower than that by the mechanical mixing method. The lowest production of acetic acid in this study, however, was obtained without $ZnCl_2$. Lu et al. provided a notable trend on the production of acetic acid with the increasing of the $ZnCl_2$ content, reporting that at the temperature of 400 °C, the acetic acid yield was only slightly increased from 1.5 wt% to 4.0 wt% of $ZnCl_2$, and then decreased as the further increasing of the $ZnCl_2$ content (Lu et al., 2011b). The result implicated that $ZnCl_2$ in its amount had a limited effect on the production of acetic acid. In the wet impregnation of this study applied 10 and 20 wt% of $ZnCl_2$, which were higher than 4 wt% of Lu et al.'s study. In general, the mechanical mixing of a catalyst would give rise to a heterogeneous and loose contact between biomass and catalyst, which results in a less $ZnCl_2$ that would take part in the reaction with biomass than applied in the mechanical mixing. Therefore, it would be possible that the acetic acid content in bio-oil is higher in the case of the mechanical mixing in this study. The reason why the pyrolysis of the corncob sample impregnated with 20 wt% of $ZnCl_2$ gave rise to a little higher acetic acid concentration compared to that impregnated with 10 wt% of $ZnCl_2$ is very hard to explain at present. One thing to mention is that the acetic acid peak in GC-FID chromatograms was asymmetrical (fronting). Therefore, it was very difficult to determine the baseline of acetic acid, especially when its peak area was very large.

The comparison between Run 5 and Run 6, where the corncob samples were both mechanically mixed with 20 wt% of $ZnCl_2$ and pyrolyzed, reveals the effect of feed rate. At a higher feed rate, the furfural concentration slightly increased; whereas the acetic acid concentration strongly decreased. A higher feed rate causes a shorter residence time (or higher flow rate of pyrolysis vapor) of pyrolysis vapor in reactor, which in turn would lessen the contact time between fine corncob particles (or pyrolysis vapor) and $ZnCl_2$. Regarding this point, the slight increase in furfural at the higher feed rate (Run 6) was somewhat strange, because the contact time with $ZnCl_2$ would be decreased in Run 6. One reason for the slight increase in furfural in Run 6 would lie in the difference in pyrolysis temperature (5 °C). As shown in Fig. 2(a), the maximum furfural concentration in bio-oil could be obtained at reaction temperatures around 350 °C. A small shift of temperature from the optimum temperature for furfural production would result in a decrease in the furfural concentration. The strong decrease in acetic acid in Run 6 was on one hand due to the relatively lower reaction temperature (353 °C), compared to Run 5 (358 °C). On the other hand, it was due to the short residence time in Run 6, which in turn, decreased the production of acetic acid.

The feed size has also a significant effect on the pyrolysis product spectrum. A smaller size would be favorable for the production of bio-oil and gas, because devolatilization of feed material would be more active with small particles due to a good heat transfer into inner part of the feed. When a catalyst is applied, a smaller feed size would help a better contact between the catalyst and feed material by increasing the surface area of the feed material. In the absence of catalyst, feed size had a little influence on the furfural production. The smaller feed size, however, led to a distinct increase in the acetic acid concentration. In the experiments with the corncob samples mechanically mixed with 20 wt% of $ZnCl_2$, a strong increase in furfural and slight increase in acetic acid were observable in Run 10 (0.25–0.425 mm), compared to the results of Run 6 (0.425–1 mm). With smaller particles, a more extensive contact between feed and catalyst could be achieved, which would be more favorable for the production of furfural than acetic acid, as in the case of the results of $ZnCl_2$ contacting methods (Fig. 2b).

Finally, Table 5 shows the yields of furfural and acetic acid from the pyrolysis of corncob, with respect to reaction parameters, the $ZnCl_2$ content and contacting method of $ZnCl_2$ with corncob.

The highest furfural yield (8.2 wt%) was obtained from the fast pyrolysis of the corncob (0.25–0.425 mm) impregnated with 20 wt% of $ZnCl_2$ at 345 °C. Meanwhile, the fast pyrolysis of the corncob (0.425–1 mm) mechanically mixed with 20 wt% of $ZnCl_2$ at 358 °C gave rise to the maximum acetic acid yield (13.1 wt%).

4. Conclusion

Fast pyrolysis of corncob was conducted to co-produce furfural and acetic acid, and the effects of reaction conditions, the $ZnCl_2$ content and contacting method of $ZnCl_2$ with corncob, on the yields of furfural and acetic acid were investigated. The bio-oil yield was 30–60 wt% of product. The main compounds of bio-oil obtained were acetic acid, hydroxyacetic acid, furfural and hydroxyacetone. The maximum furfural yield (8.2 wt%) was obtained from the corncob impregnated with 20 wt% $ZnCl_2$. The maximum acetic acid yield (13.1 wt%) was achieved by the fast pyrolysis of the corncob mechanically mixed with 20 wt% of $ZnCl_2$.

Acknowledgement

This work was financially supported by the grant from the Industrial Source Technology Development Programs (10032003) of the Ministry of Knowledge Economy (MKE) of Korea.

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